Pyrogenically produced silica

The invention provides a pyrogenically produced silica powder, the production thereof and its use.

The term fumed silica or pyrogenic silica covers all highly
5 disperse silicas which are obtained in the gas phase at high temperatures by coagulation of monomeric silica. There are two processes for the technical production of pyrogenic silicas: high-temperature hydrolysis and the electric-arc process.

10 In the high-temperature hydrolysis process, a homogeneous mixture of a vaporous silicon compound, generally silicon tetrachloride, hydrogen, oxygen and an inert gas is burnt with a burner in a cooled combustion chamber. During this process, the following reactions take place simultaneously:

15 1. $2H_2 + O_2 \longrightarrow 2H_2O$ 2. $SiCl_4 + 2H_2O \longrightarrow SiO_2 + 4HCl$
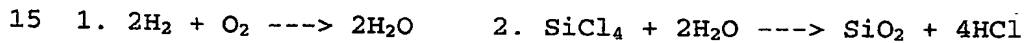
Because of the homogeneity of the gas mixture, the reaction conditions and thus the conditions for the formation and growth of each SiO_2 particle are largely identical, so that very uniform and even particles can form. In the known
20 process, air is used as the source of oxygen. The pyrogenic silicas produced by the known process have specific surfaces of between 10 and 600 m^2/g.

EP-A-759410 describes the production of a pyrogenic silica powder with a surface area of less than 90 m^2/g, preferably
25 less than 60 m^2/g, and a dibutyl phthalate number (DBP number), expressed as g of dibutyl phthalate/100 g of silica powder, of less than 60. The DBP number is a measure of the structure or the degree of fusion of the particles of the powder. A low structure is expressed by a low DBP
30 number. The silica powder described in EP-A-759410 accordingly exhibits a comparatively low structure with a comparatively low surface area. An essential feature of the process for the production of the powder is the preheating

of the mixture of silicon compound and air to temperatures
of approx. 400 degrees Celsius.

The combination of low surface area and low structure is
explained further in EP-A-1182168. Dispersions of the
5 silica powder produced there have particularly low
viscosity. The basic silica powder has little structuring.

The prior art describes silica powder with a low surface
area and with a low structure. However, it is not possible
to produce a silica powder by the processes described in
10 EP-A-759410 and EP-A-1182168, for example, which has a
similarly low surface area but is clearly more strongly
structured. A material like this could, for example, be
used where a high thickening action is desirable with a low
surface area.

15 The object of the invention thus consists in providing a
silica powder which is highly structured compared with the
prior art, with a low BET surface.

The invention provides a pyrogenically produced silica
powder, which is characterised in that it has
20   -   a BET surface of 30 to 90 m^2/g,
        -      a DBP number of at least 80, expressed as   )
               g of dibutyl phthalate/100 g of silica and
        -      a tamped density of no more than 110 g/l.

The BET surface can preferably be between 35 and 75 m^2/g,
25 and particularly preferably between 35 and 55 m^2/g. The BET
surface is determined in accordance with DIN 66131.

The DBP number can preferably be greater than 100 and
particularly preferably greater than 110. For the DBP
absorption, the force uptake, or the torque (in Nm), of the
30 rotating blades of the DBP measuring instrument is measured
on addition of defined quantities of DBP, comparable to a
titration. A sharply defined maximum is obtained for the

powder according to the invention, with a subsequent drop
at a specific addition of DBP.

The tamped density is determined on the basis of DIN ISO
787/XI K 5101/18 (not sieved). The tamped density can be
5   altered by further process steps, such as bagging or
rolling. In the powder according to the invention,
regardless of this, it is less than 110 g/l. It can
preferably be less than 100 g/l.

It can also be preferred if the silica powder according to
10 the invention has an average aggregate circumference of at
least 1000 nm. An average aggregate circumference of at
least 1200 nm is particularly preferred. The aggregate
circumference can be determined e.g. by image analysis of
the TEM images. Aggregate, within the meaning of the
15 invention, refers to primary particles of similar structure
and size which have fused together, the surface area of
which is smaller than the sum of the individual, isolated
primary particles. The term primary particles, within the
meaning of the invention, refers to particles that are
20 initially formed in the reaction and can coalesce as the
reaction progresses to form aggregates.

In addition, the kurtosis (steepness), which is a measure
of the type of distribution at the edges, of the aggregate
area of the powder according to the invention can be at
25 least 20 according to ASTM 3849-89.

The silica powder according to the invention can have a pH
value, measured in a 4% aqueous dispersion, of between 3.8
and 5.

A pyrogenically produced silica powder having a BET surface
30 of 35 to 55 m²/g, a DBP number of 100 to 130 g dibutyl
phthalate / 100 g silica and a pH value, measured in a 4%
aqueous dispersion, of 4.3 to 4.8 can be particularly
preferred.

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The invention also provides a process, which is
characterised in that at least one vaporous silicon
compound, a gas containing free oxygen (primary air) and a
combustible gas are mixed together in a closed burner and
5   then burnt in a flame in the flame tube of the burner, the
solid obtained is separated from the gas mixture and
optionally purified, wherein

- the oxygen content of the gas containing free oxygen is
  adjusted such that the lambda value is greater than or
10   equal to 1, and

- the gamma value is between 1.2 and 1.8.

Adjustment to a gamma value of 1.4 to 1.6 can preferably be
made.

In the closed burner method, the reaction mixture burns in
15   a flame tube closed to the atmosphere. By comparison, in
the open method the reaction mixture would burn in a flame
tube open to the atmosphere.

In a preferred embodiment, $1 \leq$ lambda ≤ 1.2 applies.

It is also preferred that, in addition, secondary air is
20   introduced into the flame tube, the ratio of secondary
air / primary air being ≤ 1.1.

It is also preferred that the proportion of oxygen in the
gas containing free oxygen is between 30 and 40 vol.%.

As silicon-containing compounds, silicon halides,
25   organochlorosilicon compounds or organosilicon compounds
and mixtures of the above compounds can preferably be used.
Silicon tetrachloride, methyltrichlorosilane or
tetramethoxysilane can particularly preferably be used.

In a particularly preferred embodiment of the process
30   according to the invention, it applies that $1 \leq$ lambda $\leq$
1.2, $1.2 \leq$ gamma ≤ 1.8, the ratio of secondary air /
primary air ≤ 1.1, the proportion of oxygen in the gas

containing free oxygen is between 30 and 40 vol.% and the
silicon compound is silicon tetrachloride.

The invention also provides the use of the silica powder
according to the invention for toner applications, in the
silicone and rubber industry, to adjust the rheology of
liquid systems, for the production of dispersions, as a
filler, for the film-coating of polyethylene terephthalate
and polyvinyl acetate, in lacquers and paints.

Examples

The dibutyl phthalate absorption is measured with a
RHEOCORD 90 instrument from Haake, Karlsruhe. For this
purpose, 12 g of the silica powder, to an accuracy of
5   0.001 g, are charged into a kneading chamber, this is
sealed with a lid and dibutyl phthalate is metered in
through an aperture in the lid at a preset metering rate of
0.0667 ml/s. The kneader is operated at a motor speed of
125 revolutions per minute. After reaching the maximum
10 torque, the kneader and the DBP metering are automatically
switched off. The DBP absorption is calculated from the
quantity of DBP consumed and the quantity of the particles
weighed in according to the following:

DBP number (g/100 g) = (DBP consumption in g / quantity of
15 powder weighed in, in g) x 100.

The pH is determined on the basis of DIN ISO 787/IX, ASTM D
1280, JIS K 5101/24.

The image analyses are performed using a TEM instrument
from Hitachi H 7500 and a MegaView II CCD camera from SIS.
20 The image enlargement for the evaluation was 30000 : 1 with
a pixel density of 3.2 nm. The number of particles
evaluated was greater than 1000. Preparation took place in
accordance with ASTM 3849-89. The lower threshold limit
with respect to detection was 50 pixels.

25 Lambda is the ratio of supplied oxygen in the core to
stoichiometrically required oxygen.

Gamma is the ratio of supplied hydrogen in the core to
stoichiometrically required hydrogen.

Example 1 (comparative example):

500 kg/h of SiCl$_4$ are evaporated at approx. 90°C and
transferred into the central tube of an open burner of
known design. In addition, 145 Nm^3/h of hydrogen and

5   207 Nm^3/h of air with an oxygen proportion of 35 vol.% are
fed into this tube. This gas mixture is ignited and burns
in the flame tube of the water-cooled burner. An additional
15 Nm^3/h of hydrogen are fed into an outer nozzle
surrounding the central nozzle, to avoid any caking. An

10   additional 250 Nm^3/h of air of normal composition are fed
into the flame tube. After the reaction gases have cooled,
the pyrogenic silica powder is separated from the gases
containing hydrochloric acid using a filter and/or a
cyclone. In a deacidification unit, the pyrogenic silica

15   powder is treated with water vapour and air.

Example 2 (embodiment example):

500 kg/h of SiCl$_4$ are evaporated at approx. 90°C and
transferred into the central tube of a closed burner of

20   known design. An additional 160 Nm^3/h of hydrogen and
238 Nm^3/h of air with an oxygen proportion of 34 vol.% are
fed into this tube. This gas mixture is ignited and burns
in the flame tube of the water-cooled burner. In addition,
15 Nm^3/h of hydrogen are fed into an outer nozzle

25   surrounding the central nozzle, to avoid any caking. An
additional 250 Nm^3/h of air of normal composition are fed
into the flame tube.

After the reaction gases have cooled, the pyrogenic silica
powder is separated from the gases containing hydrochloric

30   acid using a filter and/or a cyclone. In a deacidification
unit, the pyrogenic silica powder is treated with water
vapour and air.

The powders 3 to 5 according to the invention and
comparative example 6 are produced as in example 2. The

experimental conditions are given in Table 1. The
analytical data of the powders 1 to 6 are given in Table 2.

Table 1: Experimental conditions and flame parameters
calculated therefrom

Example		1	2	3	4	5	6
SiCl₄	kg/h	500	500	500	500	500	500
H₂ core	Nm³/h	145	160	190	210	240	318
Air	Nm³/h	207	238	326	371	405	500
Oxygen content of air	vol.%	35	34	34	34	34	34
Additional air (secondary air)	Nm3/h	250	250	250	250	250	250
H₂ mantle	Nm³/h	15	15	15	15	15	15
lambda		1.1	1.0	1.0	1.0	1.0	1.0
gamma		1.0	1.2	1.4	1.6	1.8	2.4

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Table 2: Analytical data of the silica powders 1-6

Example		1	2	3	4	5	6
BET	m²/g	46	43	46	50	46	96
DBP	g/100g	76	91	96	107	127	127
Tamped density[$]	g/l	53	38	33	28	25	28
pH[#]		4.5	4.5	4.7	4.7	4.8	4.6

$) direct from the process after purification step; #) 4 wt.-% disp.

Table 2 shows that the examples 2 to 5 according to the
10 invention with increasing gamma and constant lambda lead to
silica powders with approximately the same BET surface but
increasing structure (larger DBP number). At the same time,
the tamped density of the powders, determined directly from
the process, decreases as gamma increases. At gamma values
15 of more than 1.8 it was found that the desired low surface

area of the powder can no longer be achieved. Example 6
shows that, while it is true that the DBP number is > 110
g/100 g with a gamma of 2.4, this is attributable to the
clearly increased surface area.

5 With a gamma value of 1.8, the process can be operated
sufficiently economically and the resulting powders exhibit
the desired surface area and the desired degree of high
structure.

Table 3: Aggregate structure of the silica powders of
10 Examples 1, 3 and 4 by image analysis.

Ex-ample	av. area	av. circum-ference	ø(*) max	ø min	Elon-gation	Kurtosis area	SF(#)
	nm²	nm	nm	nm	nm		
1	23217	1032	292	207	1.78	14.41	39.1
3(S)	32780	1475	303	186	2.02	27.27	88.7
4(S)	29577	1447	293	179	2.01	25.38	101.1
3(&)	26217	1313	279	141	2.01	21.49	82.9
4(&)	24527	1257	259	161	2.00	24.76	97.1

*)ø = Diameter;   #) Sphericity Factor acc. to ASTM; $) Powder before
compacting; &) Powder after compacting

Figure 1 shows a circumference distribution of aggregates.
15 It shows the relative frequency (in %) with which a certain
range of the aggregate diameter (in nm) occurs in the
powder. The x-axis should be read here as: up to 1000 nm,
up to 1001 to 2000 nm, 2001 to 3000 nm etc.

A refers to the distribution of the aggregate circumference
20 of a powder not according to the invention with a BET

surface of approx. 50 m^2/g. B shows the distribution of the
aggregate circumference from the powder according to the
invention from Example 2. The clearly broader distribution
of the aggregates of the powder according to the invention
5   can be seen.